



Remarkably enhanced photocatalytic activity by nickel nanoparticle deposition on sulfur-doped titanium dioxide thin film

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ARTICLE INFO

Article history:

Received 4 July 2008

Received in revised form 26 August 2008

Accepted 26 August 2008

Available online 2 September 2008

Keywords:

Nickel nanoparticle

Titanium dioxide

Sulfur doping

Thin film

Photocatalyst

ABSTRACT

To enhance the photocatalytic performance of titanium dioxide, the structures of both bulk and surface were modified. Doping of sulfur atoms to be substituted for lattice oxygen atoms of titanium dioxide was carried out to extend the light absorption by atmosphere-controlled pulsed laser deposition, which allows direct preparation of impurity-included thin film such as sulfur-doped titanium dioxide. On the other hand, to enhance the surface catalytic reaction, nickel nanoparticles were deposited at the thin film substrate by chemical vapor reductive deposition method, which is a novel preparation technique of metallic nanoparticles on the substrate surface. Obtained sulfur-doped titanium dioxide was found to possess sensitivity to visible light with the wavelength up to 550 nm, indicating the photocatalytic activity in visible region. Sulfur doping induced the dye degradation activity under visible light irradiation. When nickel nanoparticles were deposited, a remarkable enhancement of the hydrogen evolution activity through ethanol decomposition of more than 20 times as much as unmodified titanium dioxide thin film was accomplished. In addition, the stability of sulfur atom doped into titanium dioxide structure was investigated.

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1. Introduction

Titanium dioxide is a promising photocatalyst because it is an abundant resource, chemically stable and shows high photocatalytic activity in various oxidation reactions [1]. Since Fujishima and Honda [2] discovered that titanium dioxide could electrochemically decompose water into hydrogen and oxygen under ultraviolet light irradiation, photocatalysis of titanium dioxide has attracted much attention. Among a number of photocatalytic systems on titanium dioxide, production of hydrogen is one of the most attractive processes because of the cleanness of this process. Therefore, a lot of efforts have been dedicated on hydrogen production from water [3] or organic compound [4] over titanium dioxide. However, its hydrogen evolution performance is quite low.

There are principally two approaches to enhance the photocatalytic property of titanium dioxide. One is to shift the absorption edge to longer wavelength, i.e. visible light region. Titanium

dioxide absorbs only ultraviolet light due to its wide band gap, and cannot be activated under visible light which is a main component of the solar light. A solution to expand the absorbable range to longer wavelength is to dope other elements into titanium dioxide structure. Doping of metal [5], nitrogen [6], carbon [7], sulfur [8–10] or both nitrogen and sulfur [11] as a dopant has been investigated. On the other hand, it is necessary for hydrogen evolution to keep the conduction band level of titanium dioxide itself. As known, the band gap of titanium dioxide consists of valence band formed by O 2p orbital and conduction band formed by Ti 3d orbital. The conduction band level of titanium dioxide is close to the oxidation-reduction potential on hydrogen evolution through reduction of proton. Therefore, doping of metal elements that may cause a formation of new band level in positive region is an unsuitable approach for hydrogen evolution because the newly formed level works as recombination center of photo-induced electron and hole. According to the theoretical studies [6,9], the doping of anion such as nitrogen, carbon or sulfur by substituting for the lattice oxygen of titanium dioxide is effective to narrow the band gap of titanium dioxide, and do not make any change in the conduction band level. However, large amount of nitrogen doping triggers formation of recombination center because the valence of doped nitrogen (N^{3-}) larger than that of oxygen (O^{2-}) causes

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reduced titanium cation (Ti^{3+}) in order to keep the charge balance. Therefore, among them, sulfur is regarded as the most promising candidate element, because it has the same valence as oxygen and formation of recombination centers due to the charge mismatch would be prevented. Although there have been some attempts to dope sulfur atoms into titanium dioxide fine particles [8,12], few studies [13,14] have been reported on thin film-type titanium dioxide, which has an advantage in easy handling.

Another important approach is to promote the surface reaction of the photocatalysts. The deposition of platinum [15,16], nickel oxide [17], and ruthenium oxide [18] nanoparticles on a titanium dioxide surface as hydrogen evolution active sites have been studied so far. These sites accept electrons and give them to molecules absorbed on the surface, consequently prohibiting the electron-hole recombination. According to Morikawa et al. [19], copper loading successfully promotes the photocatalytic activity of nitrogen-doped titanium dioxide particles for oxidative decomposition of acetaldehyde. On the other hand, we have proposed a novel technique, chemical vapor reductive deposition method, for metallic nickel nanoparticle preparation onto thin film substrates [20], by which we have successfully enhanced the photocatalytic activity of titanium dioxide thin film through metallic nickel nanoparticle deposition. Although works addressing the effect of metal deposition on the photocatalytic activity of titanium dioxide sensitized to visible light have been investigated, many reports deal with oxidative decomposition of organic pollutant in water or air and few reports focus on hydrogen evolution. Therefore, loading of metal on titanium dioxide should be investigated from the viewpoint of effective utilization of photo-induced electron and hole consequently for an enhancement of the photocatalytic activity.

In these regards, both to extend the wavelength region of light that titanium dioxide can absorb to generate electron and hole and to improve the activity of photocatalytic reaction taking place on the titanium dioxide surface are indispensable approaches, which can be attained by modifying the bulk as well as surface properties of titanium dioxide. Here we describe the synthesis, characterization and evaluation of a high active titanium dioxide photocatalyst thin film by sulfur doping, as well as by nickel nanoparticle deposition, at the same time.

2. Experimental

2.1. Preparation of titanium dioxide thin film

Thin film materials were prepared by pulsed laser deposition method [21], in which the inner atmospheric condition was easily controllable. Titanium dioxide powder (Wako Pure Chemicals) was pressed to mold in the shape of tablet with 10 mm diameter and 5 mm thickness, and subsequently calcined in air at 1000 °C for 4 h. Titanium dioxide target obtained in this way was rutile phase, which was identified by XRD measurement. The target was placed in a vacuum chamber which was evacuated to less than 6.7×10^{-3} Pa. For the preparation of a sulfur-doped titanium dioxide (S-TiO) thin film, carbon disulfide vapor was introduced into this chamber to control the inner pressure at 2.1 Pa. The titanium dioxide target was irradiated with a Nd:YAG pulse laser (wavelength: 1064 nm, LAB170-10, Spectra Physics) from the outside of the vacuum chamber with an incident angle of 60°. By the laser irradiation, titanium dioxide is explosively vaporized to form a thin film on a quartz glass substrate placed in the chamber. The size of the quartz glass substrate is 12 mm square and 1 mm thickness. After the laser irradiation for 50 s (500 pulses), a thin film with the thickness of ca. 50 nm was obtained. For a control, titanium dioxide thin film (U-TiO) was prepared under the initial

vacuum pressure, less than 6.7×10^{-3} Pa, without the introduction of carbon disulfide vapor.

2.2. Deposition of nickel nanoparticle

Nickel nanoparticles were deposited on the sulfur-doped titanium dioxide thin film by the chemical vapor reductive deposition method [20]. Before the deposition, a horizontal tube made of Pyrex glass was purged twice by nitrogen gas and then evacuated to less than 1.0×10^{-2} kPa. Nickelocene ($Ni(C_5H_5)_2$, Wako Pure Chemicals) as a nickel precursor was vaporized to introduce into the Pyrex glass tube to make the inner pressure 0.10 kPa. Successively, vaporized hydrazine monohydrate ($N_2H_4 \cdot H_2O$, Wako Pure Chemicals) as a reducing agent was introduced into the tube. Just after the hydrazine introduction, the inner pressure reached to 2.00 kPa. After 10 min of reaction the residual vapor was evacuated, and nitrogen gas was filled before cooling the film to room temperature. During the reductive reaction, the surface of the thin film substrate was kept at 100 °C. The absorbance spectrum of nickel deposited film was almost the same as that before the deposition, suggesting that the deposition procedure hardly affected the properties of neither S-TiO nor U-TiO thin films. Thin film materials after nickel deposition on S-TiO and U-TiO are named Ni/S-TiO and Ni/U-TiO, respectively.

2.3. Characterization of the material

A UV-vis spectrometer (UV-2550, Shimadzu) equipped with an integral sphere (ISR2200, Shimadzu) was used to measure the absorbance of the thin films. Observation with AFM (SPM9500J2, Shimadzu) was carried out to investigate the surface morphology. TEM (HF-2000EX, Hitachi) was used for identification of crystal structure. To observe with TEM, the thin film was removed from the quartz glass substrate by scratching to mount on a carbon-coated copper grid. The state of elements comprising the thin film material was analyzed by XPS (ESCA5600, ULVAC-PHI and ESCA-3400, Shimadzu). The analysis was carried out after argon ion etching. Obtained XPS spectrum was corrected using C 1s peak at 284.6 eV as a reference. Quantitative analysis for nickel, titanium and sulfur was conducted by XRF (System 3270E, Rigaku) measurement using calibration curves. Titanium, sulfur and nickel standard solutions for ICP measurement (1000 ppm, Wako Pure Chemicals) were diluted, and a certain concentration and amount of the standard specimen solution was dropped to be instilled into a filter paper (purchased from Rigaku). The each correlation between the amount of elements and the detected K α intensity was found to be well proportional.

2.4. Evaluation of photocatalytic activity

The light employed for activity test is a super-high pressure mercury lamp (BMO-500DJ (500 W) and Hx-500, WACOM R&D). For visible light irradiation, a filter (Y-45, KENKO) was used. This optical filter can absorb the light with wavelength shorter than 450 nm (the transmittance at 450 nm is 50%) and pass 90% of the incident light with the wavelength longer than 450 nm.

Two photocatalytic reactions were performed using closed batch-wise apparatus made of quartz glass. One is the hydrogen evolution by the ethanol decomposition and the other is the reductive decoloration of a dye. The former reaction was carried out in a closed glass apparatus. The glass apparatus was purged three times by argon gas and evacuated less than 1.0×10^{-2} kPa. Ethanol gas was vaporized to fill the apparatus, reaching the inner pressure to 2.7 kPa. Then, 46.7 kPa of argon was also introduced into the apparatus. Hydrogen evolved was quantified after 4 h of

lamp irradiation by a gas chromatogram with TCD (GC-8A, Shimadzu). Values were normalized by the light absorption intensity, which was obtained by subtraction the intensity of transmitted light from that of incident light using a power meter (model 407, Spectra Physics). The latter reaction was carried out in a mixture of 6 ml of methylene blue aqueous solution (2.0×10^{-5} mol dm $^{-3}$) and 0.5 ml of methanol as sacrificial acceptor for photo-generated holes [22]. Prior to light irradiation, argon purge was carried out for 10 min. The activity was estimated by the change in the absorbance at 665 nm characteristic for methylene blue, which can be decolorized also by light absorption [23]. Therefore, all results were normalized by using the absorbance of the dye solution in the absence of catalyst.

3. Results and discussion

U-TiO and S-TiO thin films were visually transparent with color of darkish blue and orange, respectively. The UV-vis absorption spectra of U-TiO and S-TiO thin films are shown in Fig. 1. The spectrum of U-TiO (Fig. 1(a)) indicates strong absorption in UV light region shorter than ca. 310 nm. It is generally known that titanium dioxide absorbs the light with the wavelength shorter than 380 nm for anatase. As mentioned in the literature [24], one presumable reason for this shorter wavelength shift is the quantum size effect. In this spectrum, a wide absorption of the light with the wavelength longer than ca. 350 nm is also observed, implying the presence of oxygen defects, i.e. Ti $^{3+}$ species in the titanium dioxide thin film [25]. Such a defect is undesirable because it works as a recombination center for photo-induced electron and hole. On the other hand, the spectrum of S-TiO thin film exhibits two kinds of absorption edges as shown in Fig. 1(b). One is in UV region attributable to the absorption of U-TiO and the other is the absorption up to 550 nm. In this spectrum, unlike U-TiO, the wide absorption in visible light region is not observed. This difference indicates that doped sulfur atoms contribute not only to visible light sensitization but also to the compensation of oxygen defects. The optical properties of nickel-deposited thin films had almost the same profiles as undeposited films, indicating that the light absorption at the nickel particles is negligible.

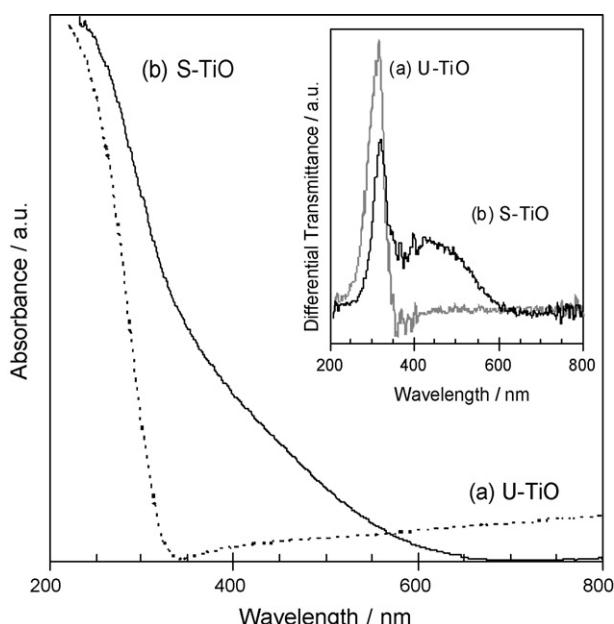


Fig. 1. UV-vis absorbance spectra of U-TiO (a) and S-TiO (b) thin films (inlet the differential transmittance spectra of the films).

As shown in Fig. 2(a), the AFM images demonstrate that the surface of U-TiO thin film has a relatively smooth surface and some island-like particles. On the other hand, the image on Ni/U-TiO (Fig. 2(b)) shows particles with the diameter between 20 and 30 nm, suggesting that nickel nanoparticles were successfully deposited on the thin film surface by the reaction of nickelocene with hydrazine. The difference in the surface morphology between U-TiO and S-TiO would be caused by the atmosphere during PLD operation. According to Syarif et al. [26], under the relatively high vacuum, titanium dioxide that explosively vaporized by laser irradiation can reach to the substrate surface without any energy loss to form smooth thin film. On the other hand, under the low vacuum such as 2.1 Pa of carbon disulfide, the energy of vaporized titanium dioxide was lessened due to collision with the atmospheric molecules, resulting in aggregative deposition of particle and formation of rough thin film. Therefore, S-TiO thin film consists of small grains with the size of ca. 30 nm or smaller (Fig. 2(c)). When nickel was deposited on S-TiO thin film, remarkable change was not observed as seen in Fig. 2(d). Judging from this result, the sizes of deposited nickel particles on S-TiO are in the range of 20–30 nm.

The S 2p XPS spectrum of S-TiO thin film is shown in Fig. 3(a). The 2p $_{3/2}$ peak around 161 eV is assigned to S $^{2-}$ species in the form of metal disulfide [27]. This indicates that sulfur atoms are successfully substituted for lattice oxygen of titanium dioxide [28]. Fig. 3(b) shows the Ni 2p XPS spectrum of Ni/S-TiO thin film, indicating that the surface was slightly oxidized by the exposure to air. The 2p $_{3/2}$ peak around 852.5 eV suggests that the nickel nanoparticle is metallic. Because peaks in Ti 2p region were also detected for the nickel-deposited thin film (Fig. 3(c)), nickel nanoparticles do not totally cover the surface of the thin film.

Fig. 4 shows the TEM bright field photographs and selected area electron diffraction (SAED) patterns of U-TiO, S-TiO and Ni/S-TiO thin films. From the bright field image, the structure of U-TiO thin film (Fig. 4(a)) is comprised of flat surface and particles with the diameter of 20 nm. The SAED pattern revealed that U-TiO thin film was crystalline [20,21]. The image of S-TiO thin film (Fig. 4(b)) demonstrates that the thin film consists of particles with the size less than 30 nm on the film surface, and any diffraction spots are not seen. In the image of Ni/S-TiO (Fig. 4(c)), on the other hand, there is no particle except thin film structure. However, the diffraction spots of Ni/S-TiO thin film can be assigned to metallic nickel, well corresponding to XPS analysis as demonstrated in Fig. 3(b).

Table 1 summarizes the results of the photocatalytic hydrogen evolution by the decomposition of ethanol on the thin films. Without irradiation and without catalyst, no hydrogen was evolved. The hydrogen evolution activity of S-TiO was higher than that of U-TiO by more than twice. It is of interest that S-TiO showed significantly high photocatalytic activity, although it has amorphous structure as mentioned in Fig. 4. It is generally known that amorphous titanium dioxide shows very low photocatalytic activity because amorphous structure has a lot of defects to cause the recombination of photo-induced electrons and holes. On the other hand, Nakamura co-workers found that nitrogen-doped titanium dioxide obtained by PLD method, which did not have long-distance order [14], showed higher photocatalytic activity than undoped sample. They concluded that the activity can be induced even by a short-distance order in the photocatalyst material. As well as it, despite the quite low crystallinity, sulfur-doped titanium dioxide thin film prepared in this study successfully gave the photocatalytic activity.

To investigate the effect of the surface morphology on the activity, a photocatalytic test using the titanium dioxide thin film prepared in argon atmosphere (denoted Ar-TiO) instead of carbon

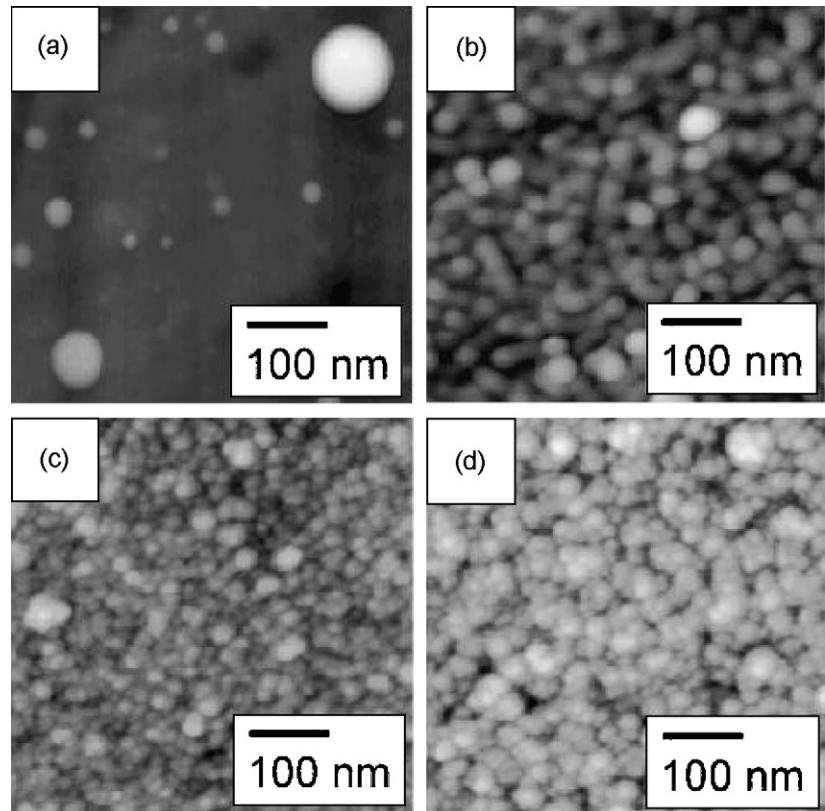


Fig. 2. AFM images of U-TiO (a), Ni/U-TiO (b), S-TiO (c), and Ni/S-TiO (d) thin films.

disulfide atmosphere was performed under the same irradiative conditions. When argon gas was introduced instead of carbon disulfide, the resulting thin film showed a rough surface morphology similar to that of S-TiO. As shown in Table 1, the activity of Ar-TiO was higher than that of U-TiO, which seems to be due to the surface morphology caused by the lower vacuum condition. On the other hand, the fact that the highest activity was accomplished on S-TiO can be convinced from the extension in photo-absorbability as shown in the UV-vis spectra rather than the effect of surface morphology. In Table 1, the relative surface areas (A_s) of the thin films are summarized. The comparison of A_s of U-

TiO with that of Ar-TiO might imply that the difference in the photocatalytic activity was caused by the surface morphology. On the other hand, because A_s of Ar-TiO was comparable to that of S-TiO, it is suggested that the enhancement of the photocatalytic activity was induced by the doping of sulfur atom into titanium dioxide.

Table 1 includes the photocatalytic activities of the nickel nanoparticle-deposited thin films. As expected, nickel deposition drastically increased the activity several times as much as Ni-free thin films. Because the effect of nickel deposition on the enhancement was more significant than that of sulfur doping,

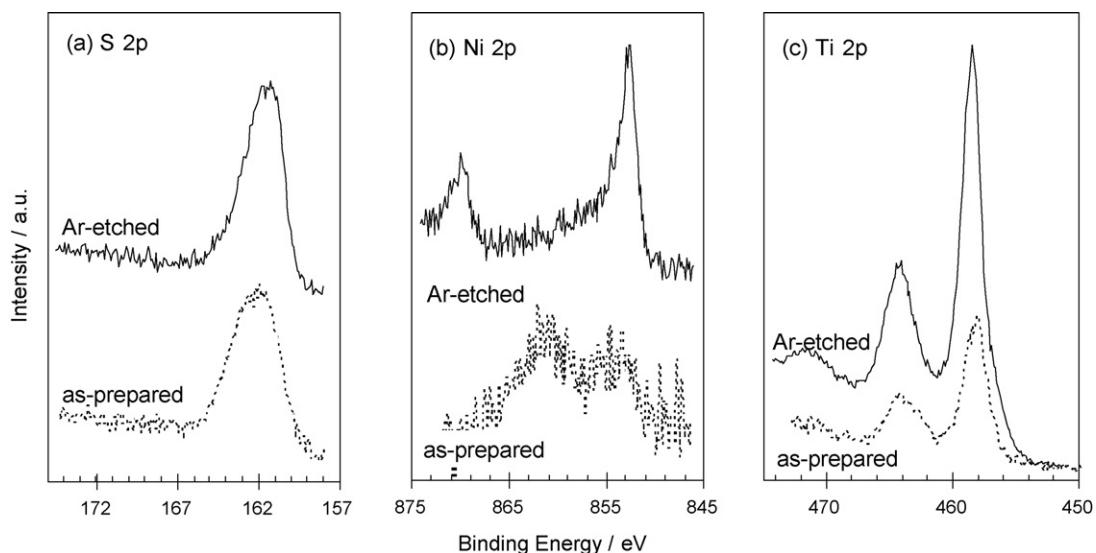


Fig. 3. S 2p (a), Ni 2p (b) and Ti 2p (c) XPS spectra of the Ni/S-TiO thin film.

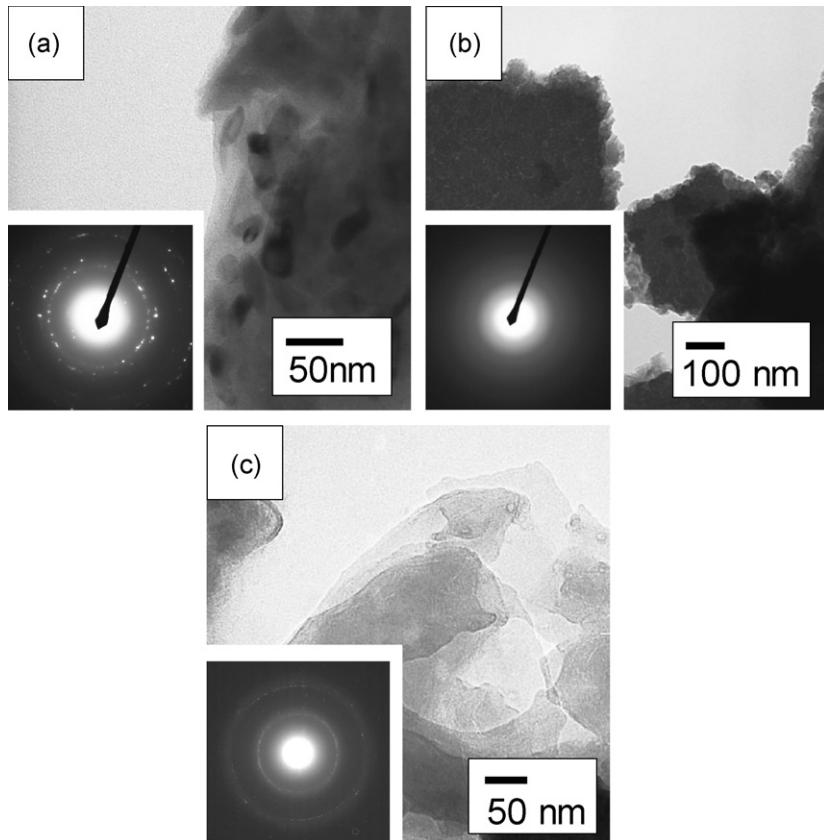


Fig. 4. TEM photographs and SAED patterns of U-TiO (a), S-TiO (b), and Ni/S-TiO (c) thin films.

the rate-determining factor of this photocatalytic reaction can be the surface reaction. In Table 1, the photocatalytic decoloration of methylene blue under visible light is also shown. Because the light irradiation was carried out using the optical filter that absorbs the light with the wavelength shorter than 450 nm, it is predictable that U-TiO, Ar-TiO, and even nickel-deposited thin film show no activity. On the other hand, decoloration of the dye successfully proceeded on the sulfur-doped thin films. Similar to the results on hydrogen evolution, nickel nanoparticles could contribute to the enhancement of the photocatalysis. This evaluation system is a reductive bleaching of methylene blue, so deposition of nickel nanoparticle as an active site for reduction reaction is a suitable approach.

To investigate the stability of the photocatalytic activity of hydrogen evolution from ethanol decomposition, cyclic tests were carried out. Fig. 5 shows the results of S-TiO and Ni/S-TiO thin

films as well as U-TiO for a control. Not only U-TiO but also sulfur-doped thin films showed stable hydrogen evolution activity without any deactivation. The average hydrogen evolution rates on U-TiO, S-TiO and Ni/S-TiO were calculated at 3.5, 9.5, and $132.4 \mu\text{dm}^3 \text{W}^{-1} \text{h}^{-1}$, respectively.

It is generally known that titanium disulfide has low stability mainly due to the elution under the light irradiation. Likewise, the photo-dissolution was observed for S-TiO, as demonstrated in Fig. 6. The S/Ti molar ratio showed a significant decrease after the first run. However, the ratio did not vary for further runs. Judging

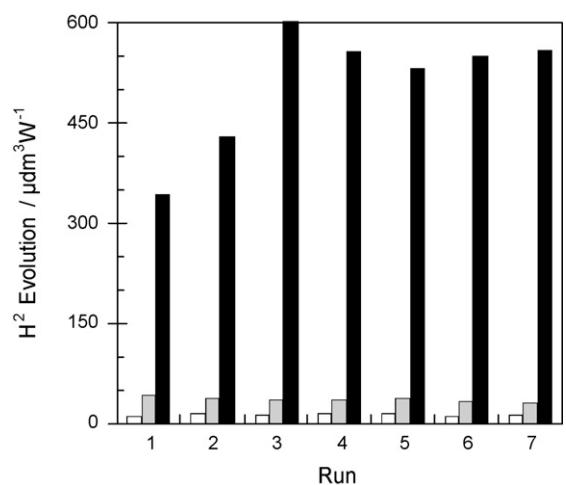


Fig. 5. Cyclic test of hydrogen evolution activity on (white bar) U-TiO (gray bar) S-TiO, and (black bar) Ni/S-TiO thin films. Each run was performed by an irradiation for 4 h.

Table 1
Photocatalytic activity of hydrogen evolution and methylene blue decoloration

Catalyst ^a	H ₂ evolution ($\mu\text{dm}^3 \text{W}^{-1}$) ^b	Methylene blue conv. (%) ^c	Relative A_s^d
U-TiO	16.8	≈0	1.00
Ni/U-TiO	98.7	≈0	1.01
Ar-TiO ^e	29.3	≈0	1.09
Ni/Ar-TiO ^e	94.1	≈0	1.05
S-TiO	40.8	2.2	1.07
Ni/S-TiO	342.7	13.4	1.14

^a The amount of thin film and Ni measured with XRF analyses is ca. 4.3 and 0.19 μg , respectively. Therefore, Ni loading is ca. 4.2 wt.%.

^b Hg light (full spectrum output) irradiation for 4 h.

^c Hg light (visible light, >450 nm) irradiation for 2 h.

^d Regarding the surface area of U-TiO as 1.00 by means of AFM.

^e Thin film prepared under Ar atmosphere of 2.1 Pa.

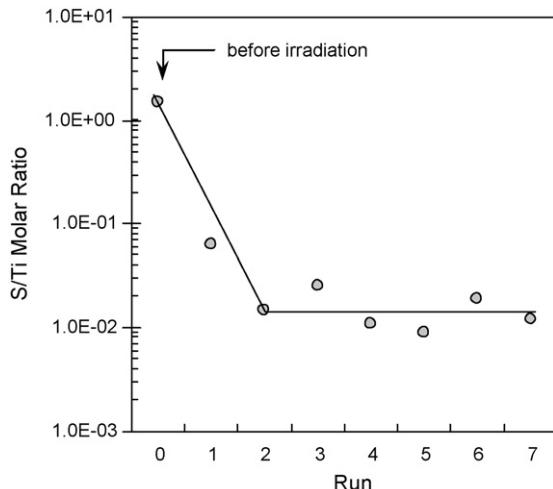


Fig. 6. Changing of S/Ti molar ratio on S-TiO thin film as a function of the light irradiation runs obtained by XRF measurement. The run number corresponds to that of Fig. 5.

from the stable activities (Fig. 5) and the constant sulfur content on S-TiO, it is suggested that sulfur atoms were introduced into the lattice of titanium dioxide to show the high hydrogen evolution activity.

As seen in Fig. 5, the activities in the first two runs on Ni/S-TiO were smaller than the following runs, where the photo-induced electrons were possibly consumed by the reduction of the nickel nanoparticles loaded on the thin film surface. Before the light irradiation, it was found that the nickel atoms near the surface of nickel nanoparticle were oxidized as mentioned in Fig. 3. After two runs, the nickel nanoparticles became metallic to work as active sites for hydrogen evolution. Those results strongly suggest that doping of sulfur atom into titanium dioxide and deposition of nickel nanoparticles onto the surface are quite effective to modify the bulk and surface structure of titanium dioxide, leading a remarkable enhancement of the photocatalytic activity.

4. Conclusion

Sulfur-doped titanium dioxide thin film was successfully prepared by atmosphere-controlled pulsed laser deposition. UV-vis and XPS studies demonstrated that sulfur atoms were substituted for oxygen atoms of titanium dioxide lattice to induce visible light sensitivity. Doping of sulfur showed a negative effect on crystallization of titanium dioxide thin film, and resulting material was amorphous, as evidenced by SAED measurement.

However, the photocatalytic activity was enhanced by sulfur doping. In addition, nickel nanoparticles deposited on the surface of thin film by chemical vapor reductive deposition method remarkably increased the photocatalytic activity in hydrogen evolution or dye decoloration.

Acknowledgement

Authors are grateful to Mr. M. Ito of IMRAM, Tohoku University and KRATOS ANALYTICAL Ltd. for the XPS measurements and meaningful comments.

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